

Chemical Speciation of Vanadium in Particulate Matter Emitted from Diesel Vehicles and Urban Atmospheric Aerosols

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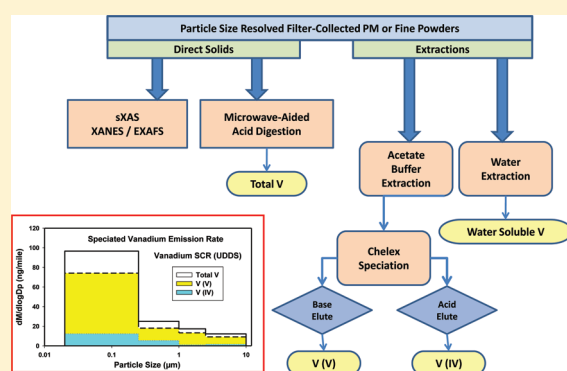
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S Supporting Information

ABSTRACT: We report on the development and application of an integrated set of analytical tools that enable accurate measurement of total, extractable, and, importantly, the oxidation state of vanadium in sub-milligram masses of environmental aerosols and solids. Through rigorous control of blanks, application of magnetic-sector-ICPMS, and miniaturization of the extraction/separation methods we have substantially improved upon published quantification limits. The study focused on the application of these methods to particulate matter (PM) emissions from diesel vehicles, both in baseline configuration without after-treatment and also equipped with advanced PM and NO_x emission controls. Particle size-resolved vanadium speciation data were obtained from dynamometer samples containing total vanadium pools of only 0.2–2 ng and provide some of the first measurements of the oxidation state of vanadium in diesel vehicle PM emissions. The emission rates and the measured fraction of V(V) in PM from diesel engines running without exhaust after-treatment were both low (2–3 ng/mile and 13–16%, respectively). The V(IV) species was measured as the dominant vanadium species in diesel PM emissions. A significantly greater fraction of V(V) (76%) was measured in PM from the engine fitted with a prototype vanadium-based selective catalytic reducers (V-SCR) retrofit. The emission rate of V(V) determined for the V-SCR equipped vehicle (103 ng/mile) was 40-fold greater than that from the baseline vehicle. A clear contrast between the PM size-distributions of V(V) and V(IV) emissions was apparent, with the V(V) distribution characterized by a major single mode in the ultrafine (<0.25 μm) size range and the V(IV) size distribution either flat or with a small maxima in the accumulation mode (0.5–2 μm). The V(V) content of the V-SCR PM (6.6 μg/g) was 400-fold greater than that in PM from baseline (0.016 μg/g) vehicles, and among the highest of all environmental samples examined. Synchrotron based V 1s XANES spectroscopy of vanadium-containing fine-particle PM from the V-SCR identified V₂O₅ as the dominant vanadium species.



INTRODUCTION

Vanadium is an air toxin and one of several metals where chemical speciation drives biological response.^{1–3} As a group 5 transition metal, vanadium can exist in a large number of oxidation states, though the IV and V species are most stable and prevalent in oxidizing environments including most biological systems. Solubility, an important determinant of biological activity, is a strong function of oxidation state, with the higher oxidation state vanadium species (IV and V) typically more soluble. Vanadium(V) species (e.g., vanadium pentoxide, V₂O₅) are considered particularly toxic with mutagenic effects, respiratory tract toxicity, and possible carcinogenic activity.^{4,5} In aqueous environments, V(IV), with a documented metalloenzyme role, may be the most biologically important species. Cohen et al.² compared several forms of vanadium and demonstrated that

solubility was an important factor associated with pulmonary immunotoxicity and that the vanadate [V(V)] species had the greatest biological impact.

Soluble vanadium speciation is a strong function of pH and at circumneutral pH V(V) exists as anionic oxyanions [V(V): (higher pH) VO₄³⁻, HVO₄²⁻, H₂VO₄⁻, H₃VO₄, VO₂⁺ (lower pH)]; while V(IV) is present as cationic VO species [V(IV): cationic (VO²⁺)]. We exploit these contrasts in aqueous chemistry in adapting, in this study, a recognized method for separation of the IV and V oxidation state species of vanadium.

Received: February 9, 2011

Accepted: November 3, 2011

Revised: September 30, 2011

Published: November 03, 2011

Vanadium is a common constituent/contaminant of atmospheric aerosols, sourced primarily from fuel oil combustion. High levels (100–1000 mg/kg) of vanadium are present in residual and fuel oils and are also found in the lubricating oils of all types of engines.⁶ Petroleum refineries are another significant source of vanadium to the atmosphere. Though many studies have documented the presence of vanadium in atmospheric aerosols,⁷ information on the chemical speciation of vanadium in primary aerosol sources and ambient aerosol is extremely limited. Our understanding of the atmospheric chemistry of vanadium, particularly redox cycling, is clearly also in its infancy,⁸ with progress severely limited by the lack of environmentally relevant speciation capable tools.

Diesel engines offer several advantages over spark ignition engines; however, NO_x [and particulate matter (PM)] emissions from diesels can be problematic and require, among other control measures, exhaust treatment to meet increasingly stringent emission standards. Vanadium-based selective catalytic reductor (V-SCR) is one of several technologies that have been developed that convert NO_x to N₂ in the presence of ammonia or urea under the oxidative conditions of a diesel exhaust, and the V-SCR technology may allow both new and retrofitted engines to meet the most stringent emission standards (Euro V and US/CARB emission targets) [refer to Supporting Information (SI)] for further details). The magnitude and chemical speciation of vanadium released to the environment from V-SCRs is poorly studied, and in this investigation, we characterized vanadium emissions from a prototype V-SCR in a retrofit application to determine if these systems may represent a new source of vanadium.

The few instrumental tools with adequate sensitivity to quantify vanadium in PM emissions from engines and particle-size-resolved ambient aerosols (e.g., ICPMS) are not speciation capable, and therefore, off-line concentration and separation or a hyphenated-instrumental approach is required to address the oxidation state of vanadium in challenging environmental samples.^{9,10} Methods employing nonselective extraction of vanadium species using resin-immobilized ligands^{11,12} or hollow fiber liquid phase microextraction¹³ have been published. Though enrichment factors of 75–200 can be obtained, to speciate, these approaches require multiple runs: one for total vanadium, and another for V(V) after complexation of V(IV) in solution. The added complexity, issues associated with subtractive methods, and inadequate sensitivity limit their utility for vanadium speciation in PM from engines, where sub-milligram PM samples and low vanadium concentrations are the norm. Sturini et al.¹⁴ used acid extraction of solids, followed by isolation of V(V) and V(IV) on Chelex, and subsequent elution of V(V) with an ammonia solution, a protocol similar in many respects to that reported here, though the use of IPC-OES severely limited their detection limits. The only generally available speciation capable reference method for V₂O₅ in aerosol PM (OSHA method ID-185 for workplace aerosols¹⁵), using XRD, requires a minimum of 20 µg of V₂O₅ for detection; clearly, this is not practical for engine/vehicle dynamometer or environmental applications.

Here we report on an integrated set of analytical tools that enable accurate measurement of total, extractable, and the oxidation state of vanadium in diesel PM and environmental samples. The analytical speciation challenge from the diesel PM was particularly difficult as the engine PM-emission samples contained total vanadium pools of only 0.2–2 ng.

METHODS

Sample Collection. Vanadium speciation was studied in PM emissions from two heavy-duty diesel trucks (HDDV) using chassis dynamometer and one medium-duty engine using an engine dynamometer. The first HDDV is a Kenworth class 8 tractor with a 1998 Cummins M11 diesel engine (11 L) operated without exhaust after treatment (Kenworth baseline), and the same vehicle equipped with two types of SCR.^{16,17} The SCR (Johnson Matthey) retrofits included a vanadium-based SCR (V-SCR) and an iron-zeolite-based SCR (Z-SCR); both SCR were run downstream of system-integrated continuously regenerating traps (CRTs) which consisted of a diesel oxidation catalyst (DOC) followed by an uncatalyzed diesel particle filter (DPF). PM emission samples were obtained under three driving cycles: (a) steady state cruise at 50 mph; (b) transient operation following the urban dynamometer driving schedule (UDDS); and (c) idle.^{17,18} Testing on the second HDDV, a Volvo class 8 tractor with a 1999 Cummins ISM engine (11 L) was designed to obtain vanadium emission and speciation data on another HDDV operated without exhaust after-treatment (Volvo-Baseline). The Volvo truck was tested only under steady state cruise mode at 50 mph with a 50% engine load.

Engine dynamometer-based samples of diesel PM from an engine exhaust train without after-treatment were also collected in studies performed at the Madison Area Technical College (MATC) engine research facility in Madison, WI.¹⁹ A 1996 model year, 3116 Caterpillar, 6.6 L medium-duty diesel engine, without EGR or DPF, was used in these tests.

Bulk (total) PM samples were collected on 47 mm Teflon filters (Pall Science 2 µm). Samples for size-resolved mass, trace element, and synchrotron-XAS characterization were collected using a Sioutas personal cascade impactor (PCIS; SKC, Inc.) at a nominal flow rate of 9 lpm. The four upper stages, >2.5 µm (coarse mode), 1.0–2.5 µm, 0.5–1.0 µm, and 0.25–0.5 µm (accumulation modes, or fine), of the PCIS were loaded with 25 mm, 2 µm, Teflon filters (Pall Science), while 37 mm, 2 µm filters (Pall Science) were employed in the pseudo-ultrafine stage (<0.25 µm). The sum of these size-fractions is effectively equivalent to a PM₁₀ size-cut. Filter samples were frozen (–20 °C) immediately after collection and remained frozen until chemical analyses were initiated. Further information on the dynamometer testing, driving cycles, test vehicle configurations, fuels, PM collection, and acknowledgments can be found in the SI.

Chemical Analysis. Our vanadium speciation strategy coupled magnetic sector ICPMS (SF-ICPMS) with off-line oxidation-state specific separations to quantify vanadium in four particle size-resolved pools: (a) total vanadium, (b) water-soluble vanadium, (c) pH 4.5 acetate soluble V(V), and (d) pH 4.5 acetate-soluble V(IV). In addition we applied focused-beam X-ray absorption near edge structure (XANES) spectroscopy to examine vanadium oxidation state and chemical speciation directly in the size-resolved engine PM. Details of the chemical speciation protocols, along with a process flowchart (Figure S1), are presented in the SI.

Extractions. Total vanadium was determined by SF-ICPMS after microwave-aided acid digestion of the PM.²⁰ Water-soluble vanadium was determined (SF-ICPMS) after extraction (and 0.22 µm filtration) of the PM in 10.0 mL of 18 MΩ MQ water. Oxidation state speciation of vanadium was determined from filtered acetate extracts (1.5 mL of 2 mM sodium acetate) of the

PM. The buffering and volume reduction are necessary for robust speciation.

Vanadium Speciation: Chemical Approach. To separate and quantify V(V) and V(IV) we adapted the method published by Wang and Sañudo-Wilhelmy in 2008,²¹ to work with the extremely small vanadium masses available from the PM extractions. The approach relies upon the retention of the dominant chemical forms of both oxidation state species in the pH range 4–7.4, on Chelex. At high pH, however, Chelex acts as a cation exchanger, and the V(V) species, which are anionic at high pH, can be selectively eluted. The method is outlined below; refer to SI for details.

- PM samples are extracted with 1.5 mL of 2 mM (pH 4.5) sodium acetate in nitrogen-purged, acid cleaned, screw-capped polypropylene vials. A 1 h extraction period with continuous agitation (under nitrogen flushed canopy) in the dark at room temperature is used.
- Polypropylene columns (1.5 mL) of acid cleaned Chelex-100 resin are prepared just prior to sample extraction. Columns are flushed with 4.0 mL of MQ and then buffered with 0.3 mL of 0.1 M sodium acetate to bring the resin pH to 4.5.
- Sample extract (1 mL) is placed onto the column and eluted at a flow rate of 1 mL/min. This column passing fraction contains vanadium species not retained by the Chelex resin.
- The column is successively eluted, again at 1.0 mL/min, with four 1.0 mL volumes of 0.1 M ammonium hydroxide. This fraction contains the V(V) species.
- The V(IV) species are eluted from the column with two successive 1.0 mL aliquots of 0.2 M perchloric acid.

Vanadium Speciation: XANES Spectroscopy. Synchrotron-based XANES spectroscopy of size-resolved diesel PM was performed at the microprobe beamline 10.3.2 (Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA). Particles containing vanadium were identified by X-ray fluorescence mapping using a focused beam (5 μm^2 spot on the sample). V 1s spectra were then collected over the energy range 5350–5720 eV in fluorescence mode. Experimental spectra were compared to a spectral library of 19 vanadium-bearing materials. Principal component analysis, target transformation analysis, and linear least-squares fitting were accomplished using ALS BL10.3.2 custom software and the software program SixPack. The SI provides additional details of the XANES analysis.

■ RESULTS AND DISCUSSION

Chelex Speciation Method Performance. A synopsis of key method performance metrics are provided here; further details are presented in the SI. Procedural blanks measured over a several month evaluation period ($n = 12$) averaged 4 ± 3 pg for V(V) and 10 ± 9 pg for V(IV), resulting in 3σ detection limit (DL) estimates of 9 and 27 pg for V(V) and V(IV), respectively. The rigorous control of blanks, application of SF-ICPMS, and miniaturization of the processing protocols resulted in analytical detection limits that are improved by factors of 2–10 over similarly calculated metrics reported²¹ for a Chelex-based vanadium speciation method targeted at seawater, and represent orders-of-magnitude enhancement in DLs over published vanadium speciation approaches for freshwater and aerosols.^{9,10,14,15} Other performance metrics (see below) indicate that the method is robust at picogram to nanogram levels of vanadium. Sampling

10 m³ of air would result in 3σ DLs of 1 and 3 pg m⁻³ for V(V) and V(IV), respectively.

Chelex columns were challenged with vanadium compounds of specific oxidation state to confirm the selectivity of the speciation protocols (Figure S2). The masses of vanadium used were in the low nanogram range to improve the relevance of the outcomes to real-world samples. In experiments with V(V) (V₂O₅) an average of 95% ($n = 7$) of applied V(V) was recovered as V(V), while in challenges with V(IV) species (VO₂ and VOSO₄), an average of 86% ($n = 13$) was recovered as V(IV).

Vanadium stability studies carried out by Wang and Sañudo-Wilhelmy²¹ indicated that V(IV) was stable for a 4 h period at pH 4.5, and that only minor (few percent) oxidation of V(IV) occurs during processing, generally consistent with our observations. The stability of V(V) and V(IV) in more complex environmentally relevant matrices was evaluated in spiking studies to ascertain whether changes in redox state may occur during the extraction as a result of interaction with matrix components. Two types of systems were evaluated: (a) filtered extracts of both standard reference materials (SRMs) and roadway dusts, and (b) heterogeneous suspensions of roadway and engine emission particulates. In both the filtered extracts and particle-laden systems, recovery of V(V) spikes was near quantitative, with over 95% of the spike recovered as V(V). Spike recoveries of V(IV) in these complex matrices exhibited more variation, but no systematic problem was identified, with measured recoveries in the 91–102% range.

Total retention percentages of defined vanadium standards on the Chelex columns of all compounds tested were >95% ($n = 24$), and mass balances were, within error, quantitative. For the engine emission PM extracts, mass balances ranged from 92% to 126% (mean = 106%, $n = 34$), and column retention (i.e., V(V) + V(IV)) from 71% to 98%.

Precision of the Chelex oxidation state speciation method was assessed from measurements of replicate standards, and replicate samples were used to evaluate the overall (sample extraction and Chelex processing) method precision. For defined standards (1–30 ng total V) precision was typically in the 5–15% RSD range (Figure S2) and in the range 2–20% RSD for environmental samples and reference materials (0.2–11 ng V; Figure S4), though the uncertainty of trace components can be much larger. These precision metrics are comparable to that reported by Wang and Sañudo-Wilhelmy,²¹ though in this study we are working at concentrations an order of magnitude lower. The high sensitivity of the method and performance with sub-nanogram (<0.25 ng) vanadium masses are illustrated in Figure S3 for the trace quantities of vanadium available from size-resolved engine PM samples where precision of ± 2 –3% for V(V) and ± 2 –4% RSD for V(IV) was measured.

Diesel Engine PM Speciation: Particle-Size Aggregated Total, Water, and Acetate Soluble Vanadium Emission Rates. Total and water-soluble vanadium emission rates (tunnel blank corrected ng/mile), calculated from the sum of the measured rates in each of the 5 PCIS size-fractions, are presented in Figure 1A and detailed in Table S1 (SI). Total PM emission rates are also listed in Table S1 for reference. Under UDDS conditions the total vanadium emission rate from the V-SCR configured vehicle (206 ± 17 ng/mile) was 4-fold greater than that from the Z-SCR (55 ± 12 ng/mile) equipped vehicle. Substantially greater (10–13-fold) emission of titanium was also observed with the V-SCR, indicating possible release of catalyst metals from the tested prototype system. Size-resolved (PCIS) tests of the V-SCR under vehicle cruise conditions were

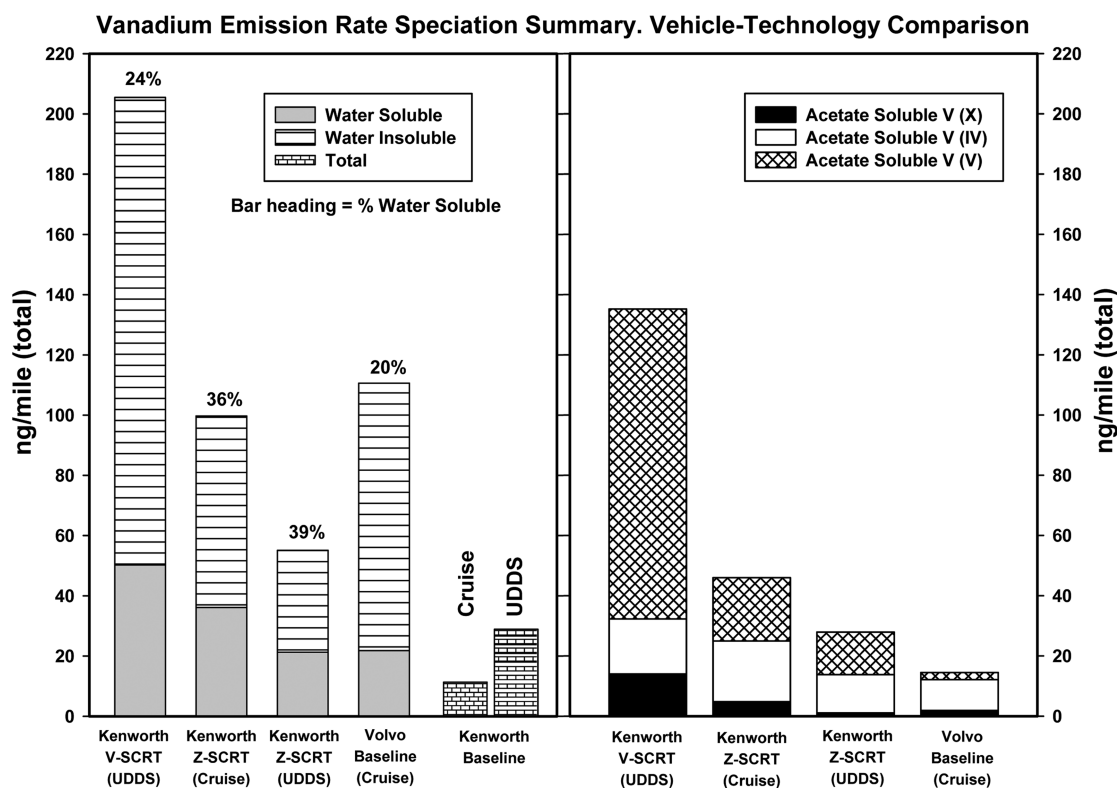


Figure 1. Vanadium emission rate speciation summary. Vehicle-technology comparison. Particle size integrated (PM₁₀) emission rates expressed in ng/mile. (A) Water-soluble and water-insoluble species. (B) Acetate soluble oxidation state speciation. V(x) = not-retained.

unsuccessful due to instrument failure; however, Hu et al.¹⁷ reported a nearly 3-fold increase in total (TSP) vanadium emission rate under cruise as compared with UDDS conditions with the V-SCR. In that study nearly every other element exhibited a reduction in total (TSP) emission rate under cruise as compared with UDDS conditions with the V-SCR. The conspicuous exceptions were V, Ti, and S which showed significantly increased (factors of 2.7, 7.9, 2.0 respectively) emission rates under cruise, implicating the V-SCR as the source of these metals and suggesting a substantive impact of exhaust/catalyst temperature on vanadium emissions from the V-SCR. Exhaust temperature (425 °C engine out and 372–376 °C post V-SCR for cruise and 276 °C engine out and 191–363 °C post V-SCR for UDDS) is likely a major driver of the mechanism and magnitude of release of catalyst material, e.g., through enhanced volatility and/or more favorable conditions for V oxidation at the higher temperatures. Stochastic release from mechanical vibration of the friable catalyst is also a potential factor. Under cruise conditions the total vanadium emission rate of the Zeolite SCR (99.7 ± 11 ng/mile) configured vehicle was nearly double that measured under UDDS conditions. The total emission rate of vanadium from the Volvo baseline vehicle (no SCR) running under cruise conditions (111 ± 27 ng/mile, Figure 1A) was not significantly different than that from the Z-SCR under the same driving cycle. Baseline (no SCR) vanadium emission rates (TSP) (Figure 1A) in the Kenworth vehicle of 28.9 ± 9.7 and 11.3 ± 4.8 ng/mile (UDDS and cruise, respectively) were measured by Hu et al.¹⁷ Our measured total vanadium emission rate from the V-SCR configured vehicle represents a 7-fold increase over the Kenworth UDDS baseline and a 2-fold increase over the Volvo (cruise) baseline. The general similarity of the UDDS emission rates of the

Kenworth baseline and Z-SCR vehicle configurations suggests that lube oil is a major contributor to the vanadium emissions from the Z-SCR.

Subtracting the Kenworth UDDS baseline emission rate (Hu et al.¹⁷) from the V-SCR rate results in a V-SCR emission increment of 177 ± 20 ng/mile, or 86% of the total emission rate, and 6-fold greater than the baseline value.

These dynamometer-measured total vanadium emission rates for the engines without after-treatment are 1–3 orders of magnitude lower than those determined in field road-way tunnel-based studies. For example, Lough et al.²⁰ reported PM₁₀ vanadium emission rates ranging from 320 to 3700 ng/mile in studies carried out in road-way tunnels in Milwaukee, WI, and Handler et al.²² reported a PM₁₀ emission rate of 4800 ng/mile from the Kaisermühlen-tunnel in Austria. The dynamometer laboratory is a controlled, idealized setting, and on-road fleet contrasts (e.g., smokers) and uncharacterized nonengine sources of vehicular vanadium likely contribute to this difference in total vanadium emission rates between the dynamometer and on-road measurements. Total (but not V(V)) vanadium emission rates from the V-SCR are, in general, also significantly lower than those determined in tunnel studies.

The water-soluble vanadium emission rates for the Volvo baseline (22 ± 5 ng/mile) and Z-SCR-equipped vehicles (21 ± 7, UDDS, and 36 ± 6, cruise ng/mile) were all similar (Figure 1A). The relatively uniform water-soluble vanadium emissions rate across vehicle configurations suggests the presence of a defined mobile species/pool of vanadium in the source, again, possibly the lube oil. In aggregate, 20–25% of total V was measured as water-soluble in the PM from the V-SCR and Volvo baseline vehicles, with a significantly greater soluble component in the

Z-SCR-tested vehicles (36 and 39%, cruise and UDDS respectively, Figure 1A): differences largely driven by variation in the water insoluble component.

The acetate (pH 4.5) soluble vanadium generally trended with the total and water-soluble emissions (Figure 1B), though substantive differences were apparent. While the acetate-soluble fraction was consistently greater than the water-soluble fraction in the SCR-equipped vehicles, the percentage of total vanadium emission that was acetate soluble in the V-SCR (65%) was greater than that measured in the Zeolite SCRs (45% and 54%, cruise/UDDS respectively); i.e. the vanadium species emitted from the V-SCR catalyst exhibits greater acetate solubility than vanadium derived from the baseline vehicle or from Z-catalyst-processed vanadium. In contrast with the SCR-equipped vehicles, the acetate soluble vanadium fraction in PM from the Volvo baseline vehicle was not significantly different than the water-soluble fraction, and at just 13% of total, the lowest soluble fraction measured in this study. The vanadium species in the emission increment produced and/or processed by the SCRs appears to have limited water solubility, but is more soluble in pH 4.5 acetate. As discussed later, this difference is related to the oxidation state speciation of the emitted vanadium.

Diesel Engine PM Speciation: Oxidation State Speciation of Particle-Size-Aggregated Acetate Soluble Vanadium. The particle-size-integrated oxidation state speciation of acetate soluble vanadium in PM from the studied vehicle configurations is presented in Figure 1B. The measured emission rates of acetate soluble V(IV) exhibited only relatively small variation between the vehicle configurations, ranging from 10.2 ng/mile in the Volvo baseline (no-SCR) to 20.1 and 12.7 ng/mile in the Z-SCR (cruise and UDDS, respectively), to 18.3 ng/mile in the V-SCR. The V(IV) species represented the large majority (71%) of total vanadium emissions from the baseline Volvo vehicle, with only a small contribution from the V(V) species (16%). This species distribution was substantiated in the other baseline diesel engine tested (Caterpillar), where we measured 62% V(IV) and 13% V(V) in the acetate extracts. Thus, from $2/3$ to $3/4$ of vanadium emissions in diesel PM from baseline vehicles (i.e., without after-treatment) is in the V(IV) species.

The speciated vanadium measurement in PM from baseline exhausts underscores the sensitivity of the method where between 18 and 64 pg of total soluble vanadium was speciated in 6 separate trials. A majority of the acetate soluble vanadium fraction from all vehicle configurations, except the V-SCR, is represented by V(IV) species. Vanadium in lubricating oil is associated with porphyrins and other organometallic compounds, existing primarily in the V(III) or V(IV) oxidation state. The measured vanadium speciation in the PM from the engine without exhaust after-treatment (and to a large extent the Z-SCR) is consistent with this feed-stock speciation, and also with the partial oxidation expected in the combustion train.

In contrast to V(IV), the emission rate and fraction of V(V) varied dramatically between the studied vehicle configurations. Measured emission rates of acetate soluble V(V) ranged from 2.3 ng/mile in the baseline vehicle to 21.0 and 14.1 ng/mile in the Z-SCR configurations (cruise and UDDS, respectively) to 103 ng/mile in the V-SCR equipped vehicle. This V-SCR V(V) emission rate is 44-fold greater than that observed in the Volvo baseline vehicle. Overall, 76% of acetate soluble vanadium in PM from the V-SCR equipped vehicle was present as V(V), compared with 46% and 50% in the Z-SCR (cruise and UDDS, respectively) configured vehicles and 16% in the baseline vehicle.

Subtracting the baseline (Volvo) V(V) and V(IV) emission rates from the rates measured from the SCR-equipped vehicles provides estimates of the oxidation-state specific vanadium emission increment for the tested SCRT technologies. Nearly 93% (109 ng/mile) of the total increment in acetate soluble vanadium from the V-SCR was present as V(V), while the V(V) fraction in the emission increment from the Z-SCR (28.6 and 14.1 ng/mile; cruise and UDDS, respectively) was lower (65% cruise and 82% UDDS), though relatively high. Whether the V(V) increment from the Z-SCR reflects a native V(V) source species or oxidation of a V(IV) source is difficult to determine.

If one applies the measured V(V) fraction of 15% in acetate extracts of PM from vehicles without after-treatment to the on-road fleet in general and also assume that 25% of total vanadium is soluble (Figure 1) and equate these factors to published on-road (tunnel-derived) emission rates, one arrives at soluble V(V) emission rates in the range 12–180 ng/mile. These fleet average soluble V(V) emission rate estimates are comparable to the measured rates (103 ng/mile) from the dynamometer experiments with the prototype V-SCR. The regional/global implications of these findings will clearly depend upon the magnitude of nonmobile (and off-road mobile) sources of V(V) to the environment.

Diesel Engine PM Speciation: Particle-Size Resolved Speciation. Two modes are apparent in the particle size distributions of speciated (IV, V, total) acetate soluble vanadium in PM from three vehicle configurations (V-SCR, Z-SCR-cruise, Z-SCR-UDDS), with a clear contrast between the size-distributions of V(V) and V(IV) (Figure S5). The V(V) distribution is characterized by a major single mode in the pseudo-ultrafine size range, consistent with a high-temperature semivolatile emission process. On average nearly 80% of acetate soluble V(V) is found in the $<0.25\ \mu\text{m}$ size-cut (Table S1) and with essentially all of the V(V) emission increment from the V-SCR present in the pseudo-ultrafine. In contrast with V(V), the acetate soluble V(IV) size distribution is either relatively flat or characterized by a maxima in the accumulation mode ($0.5\text{--}2.5\ \mu\text{m}$), likely reflecting a dominant mechanical loss process. The influence of temperature on vanadium oxidation state/size distribution is also apparent within the Z-SCR trials, with a small pseudo-ultrafine mode ($<0.25\ \mu\text{m}$) present in the higher temperature ($425\ ^\circ\text{C}$) cruise profile but not in the lower temperature ($276\ ^\circ\text{C}$) UDDS profile (Figure S5). Thus, it appears that the vanadium oxidation states have unique particle size distributions and are potentially diagnostic of loss mechanisms. The size distributions of summed (V + IV) acetate soluble vanadium are consistent with the slightly more resolved (not every size fraction was speciated) measured total (microwave digestion) vanadium distributions, with the two modes clearly resolved (Figure S6). The size distributions of water-soluble V species for all non-V-SCR and baseline vehicle configurations were very similar in structure (mostly flat with a minor accumulation mode), suggesting a common V source (engine lube oil), dominated by V(IV)^{8,23} (Figure S6).

Within a given after-treatment, we do not observe a statistically significant particle size dependency of acetate soluble vanadium speciation; e.g., in the V-SCR equipped vehicle the V(V) fraction ranged from 72% in the $0.25\text{--}1\ \mu\text{m}$ size-cut to 77% in the $<0.25\ \mu\text{m}$ size cut, and in the Z-SCR the V(V) fractions all fall within a narrow range, from 42% ($2.5\text{--}10\ \mu\text{m}$) to 57% ($<0.25\ \mu\text{m}$) for the cruise driving cycle and from 49% ($0.25\text{--}1\ \mu\text{m}$) to 52% ($0.25\ \mu\text{m}$) for the UDDS driving cycle (Table S1).

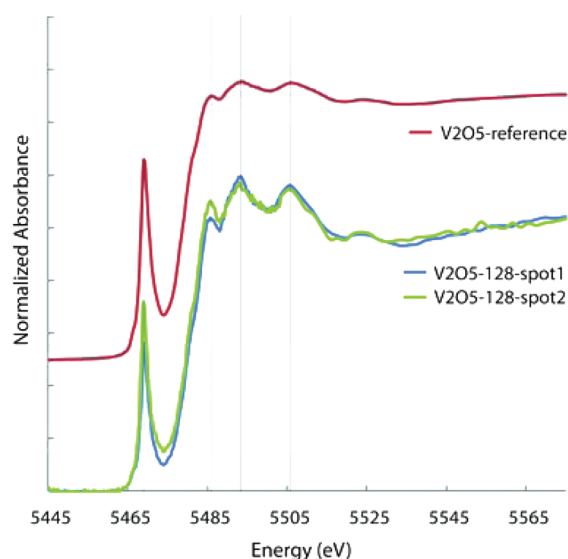


Figure 2. Vanadium pentoxide particles were identified in the fine particle fraction in PM from the engine fitted with the V-SCR. Vanadium 1s XANES spectra from two V-rich particles are plotted along with a pure V_2O_5 reference spectrum. Particles impacted on an aluminum substrate (sample code V_2O_5 -128).

Diesel Engine PM Speciation: PM Mass-Normalized Vanadium Composition. PM mass-normalized levels of total vanadium (Figure S7) from the V-SCR ($14.3 \mu\text{g/g}$) were 14-fold greater than in PM from the baseline vehicle ($0.98 \mu\text{g/g}$). The acetate soluble V(IV) content of the PM showed only minor variation across SCR technologies and driving cycles (1.2 – $1.6 \mu\text{g/g}$) and represents a 20-fold increase over acetate soluble V(IV) levels in the baseline vehicle ($0.07 \mu\text{g/g}$). The V(V) content of the V-SCR ($6.6 \mu\text{g/g}$) was radically greater (400-fold) than that in PM from baseline ($0.016 \mu\text{g/g}$) and Z-SCR ($1.6 \mu\text{g/g}$) configured vehicles. Further discussion of the PM-mass normalized data is presented in the SI.

Diesel Engine PM Speciation: XANES Characterization. The XANES analysis provides important complementary data to the soluble vanadium speciation, directly probing the insoluble (as well as soluble) vanadium components of the PM (60–80% of the vanadium was water insoluble and 35–85% was acetate insoluble). Vanadium 1s XANES spectra can be used to discriminate among vanadium 2+, 3+, 4+, and 5+ materials. Vanadium XANES spectra are also sensitive to crystal structure, and one can distinguish between two V(5+) materials, sodium vanadate (NaVO_3) and vanadium pentoxide (V_2O_5)²⁴ (Figure S8).

Vanadium pentoxide particles were identified in vanadium-containing fine-particle PM from the V-SCR (sample code V_2O_5 -128). Vanadium 1s XANES spectra from the V-rich particles are in good agreement with the pre-edge amplitude, shape, and energy position of vanadium pentoxide (Figure 2). In addition, the particles exhibit the distinctive three resonance peaks of vanadium pentoxide.²⁵ Taken together, the Chelex-based and XANES characterizations clearly indicate that V_2O_5 from the catalyst of the prototype retrofit SCR is being released in the fine and pseudo-ultrafine PM. The vanadium speciation of the coarse PM fraction is much more complex than the fine fraction, with multiple vanadium species observed, including V(2+), V(3+), V(4+), and V(5+) phases, but very little V_2O_5 (Table S3;

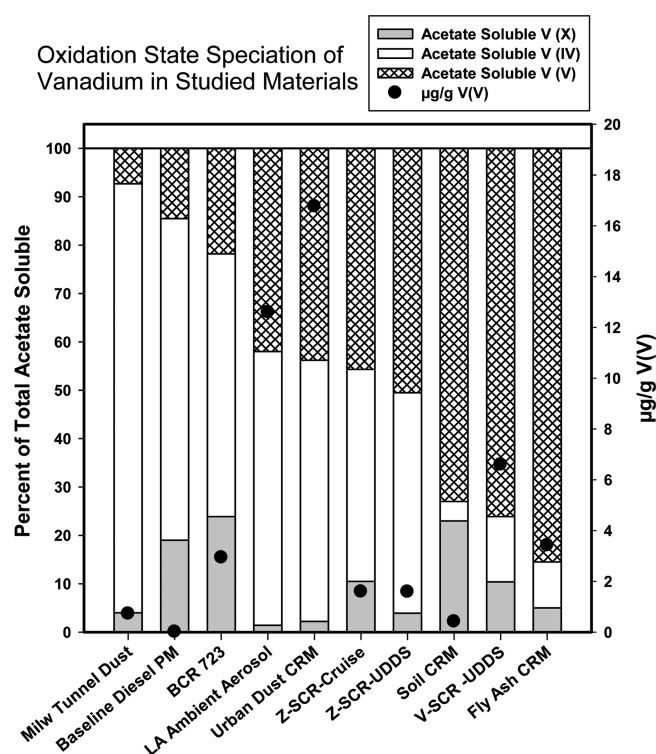


Figure 3. Summary of vanadium oxidation state speciation of studied materials. Bars show distribution of vanadium V(V) and V(IV) as a percent of total acetate soluble vanadium and points show $\mu\text{g/g}$ V(V) in the particulate materials. V(x) = not-retained.

Figure S9). The chemical heterogeneity of the coarse PM is larger than our reference spectral library can accommodate as indicated by mismatches between best fits and experimental spectra for several particles (Figure S9). The coarse fraction (a small component of total vanadium emissions from the V-SCR) likely reflects vanadium species emitted via more mechanical loss processes and therefore captures a spectrum of species from the Rideal-Eley V-SCR cycle. The water solubility of vanadium in the coarse PM was lower than in finer fractions, consistent with the XANES speciation, i.e., the relatively low concentrations of the more soluble V(5+) species.

Vanadium-bearing particles in the coarse PM from the Z-SCR had uniform vanadium speciation [30–50% vanadate (5+) and 50–70% vanadium dioxide (4+), Figure S10], findings in close agreement with that from the Chelex speciation. No V_2O_5 is observed in the PM from the prototype Z-SCR.

Comparison of Vanadium Speciation in Engine PM with That in Environmental Materials. The vanadium oxidation state distribution in acetate extracts of the diesel engine PM is compared with that measured in a selection of environmental materials in Figure 3. Also presented in Figure 3 is the mass-normalized content of V(V) in these materials. The average fraction of V(V) determined in the baseline (no SCR or DPF) diesel PM extracts (13–16%) is comparable to that determined in roadway tunnel dusts [$7 \pm 2\%$ and $22 \pm 1\%$ in Milwaukee and Austria (BCR 723) respectively, Figures 3 and S4]. The similarity of the V(V) fractions in roadway dusts and engine PM is consistent with a vehicular source for the vanadium in these dusts and also indicates that the speciation is relatively stable. The measured fraction of V(V) in ambient atmospheric aerosols

in the LA basin ($41 \pm 3\%$) was essentially identical to that determined in the NIST Urban Dust CRM ($42 \pm 3\%$), both significantly greater (2–3 fold) than the V(V) fraction in road-way emissions. These ambient PM vanadium speciation data are suggestive of a significant nonvehicular source of V(V) or substantial redox processing of vanadium in the atmosphere. A recent study²⁶ hints at the potential involvement of vanadium redox chemistry in the oxidation of SO₂ and resultant reduction of V(V) to V(IV). Photochemically driven reduction is also possible. Very large acetate soluble V(V) percentages were measured in the NIST Fly Ash CRM-1633 (80–92%) and NIST Soil CRM-2709 (76%) acetate extracts, comparable to that in the V-SCR PM (Figures 3 and S4). Further discussion of the CRM data is presented in the SI. The intrinsic level of acetate labile V(V) in PM from the V-SCR (6.6 $\mu\text{g/g}$) is among the highest of the materials evaluated, exceeded only by the Urban Dust CRM and LA Ambient Aerosol (Figure 3). Studies of comparable scope on additional SCR-equipped vehicles are in development.

■ ASSOCIATED CONTENT

S Supporting Information. Details of sample collection, chemical analysis, method performance, XANES spectroscopy, and additional examples/discussion of vanadium speciation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ ACKNOWLEDGMENT

We thank M. Marcus for invaluable support at ALS BL 10.3.2 and L. Briscoe for help with data collection. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract DE-AC02-05CH11231.

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